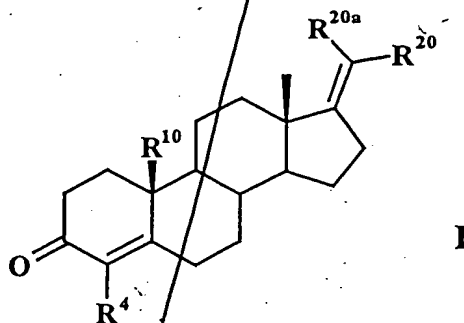


## Claims

1. 17-Methylene steroids of general formula I



in which

R<sup>4</sup> stands for a halogen atom or a pseudohalogen,

R<sup>10</sup> stands for a hydrogen atom or a straight-chain or branched C<sub>1</sub>-C<sub>4</sub> alkyl group,

R<sup>20</sup> and R<sup>20a</sup>, independently of one another, represent a hydrogen atom, a straight-chain or branched C<sub>1-4</sub> alkyl or hydroxy-C<sub>1-4</sub> alkyl group, or

one of radicals R<sup>20</sup> and R<sup>20a</sup> means a hydrogen atom, a straight-chain or branched C<sub>1-4</sub> alkyl or hydroxy-C<sub>1-4</sub> alkyl group, and the other radical means a halogen atom or a pseudohalogen.

2. 17-Methylene steroids according to claim 1, characterized in that R<sup>4</sup> stands for a chlorine or bromine atom or a cyano group.

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**DECLASSIFICATION AUTHORITY**  
 1. **DATE** 11/11/2011  
 2. **BY** 60322  
 3. **REASON** 25X(1)  
 4. **APPROVED** [Signature]  
 5. **DATE** 11/11/2011

1) E-17-Chloromethylene-4-chloro-estr-4-en-3-one,

2) E-17-Cyanomethylene-4-chloro-estr-4-en-3-one,

3) Z-17-Cyanomethylene-4-chloro-estr-4-en-3-one,

4) Z-17-(1')-Cyanoethylidene-4-chloro-estr-4-en-3-one,

5) Z-17-Ethylidene-4-chloro-estr-4-en-3-one,

6) E-17-Ethylidene-4-chloro-estr-4-en-3-one,

7) E-17-Bromomethylene-4-chloro-estr-4-en-3-one,

8) Z-17-Chloroethylidene-4-chloro-estr-4-en-3-one,

9) Z-17-Bromoethylidene-4-chloro-estr-4-en-3-one,

10) E-17-Chloromethylene-4-cyano-androst-4-en-3-one,

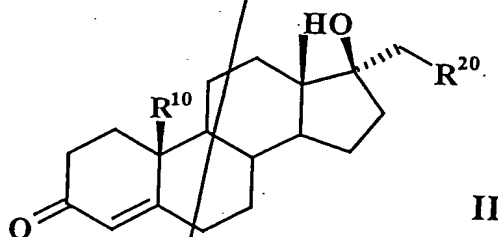
11) E-17-Chloromethylene-4-chloro-androst-4-en-3-one,

12) E-17-(2')-Hydroxyethylidene-4-chloro-estr-4-en-3-

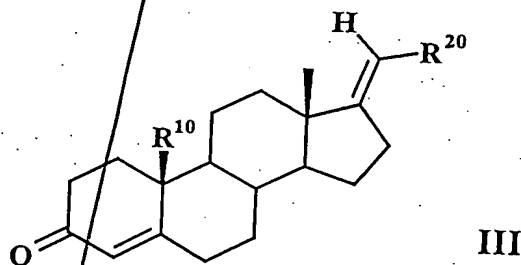
one and

13) Z-17-(2')-Hydroxyethylidene-4-chloro-estr-4-en-3-one.

6. Process for the production of 17-methylene steroids according to claim 1, in which  $R^{20a}$  means a hydrogen atom, wherein a compound of general formula II,



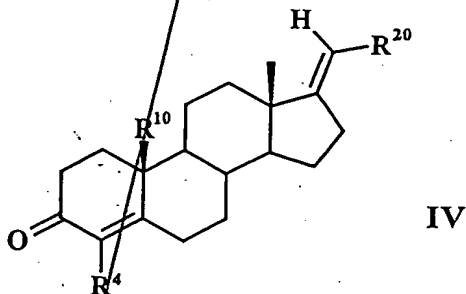
is reacted in an aprotic solvent with an acid chloride to a 17-methylene steroid of general formula III,



the 4,5-epoxide is generated with  $H_2O_2/NaOH$ , the 4,5-epoxide is then opened with a nucleophilic reagent, which is derived from a halogen atom or pseudohalogen, in a dipolar aprotic solvent to a halogen- or pseudohalogen hydrin, and optionally reacted with mineral acid, carboxylic acid or

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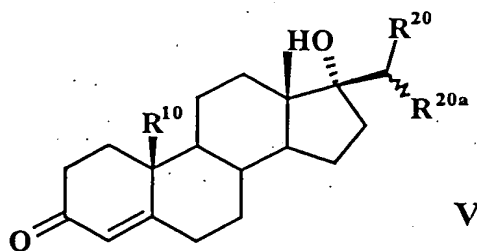
sulfonic acid in a protic or aprotic solvent with dehydration to a compound of general formula IV, in which



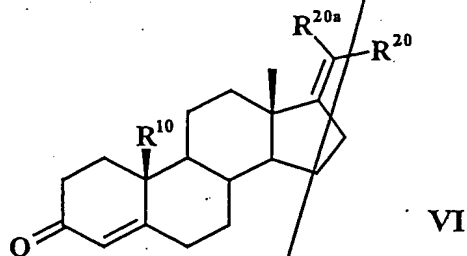
*Sub B1*

R<sup>4</sup> stands for a halogen atom or pseudohalogen, whereby R<sup>10</sup> has the meaning indicated in claim 1, and R<sup>20</sup> means a C<sub>1-4</sub> alkyl or hydroxy-C<sub>1-4</sub> alkyl group, a halogen atom or a pseudohalogen.

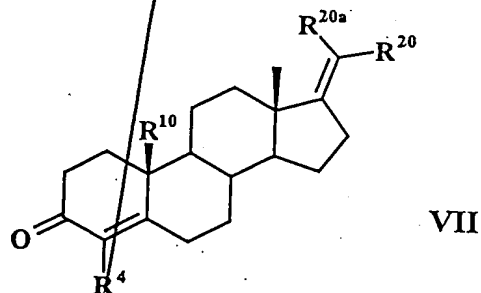
7. Process for the production of 17-methylene steroids according to claim 1, wherein a compound of general formula V,



is reacted with an acid chloride in an aprotic solvent to a methylene steroid of general formula VI,



the 4,5-epoxide is generated with  $\text{H}_2\text{O}_2/\text{NaOH}$ , the 4,5-epoxide is then opened with a nucleophilic reagent, which is derived from a halogen atom or pseudohalogen, in a dipolar aprotic solvent to a halogen- or pseudohalogen hydrin, and optionally reacted with mineral acid, carboxylic acid or sulfonic acid in a protic or aprotic solvent with dehydration to a compound of general formula VII,



in which  $\text{R}^4$  stands for a halogen atom or pseudohalogen, whereby  $\text{R}^{10}$  has the meaning indicated in claim 1, and  $\text{R}^{20}$

*Sub B*  
means a C<sub>1-4</sub> alkyl or hydroxy-C<sub>1-4</sub> alkyl group, and R<sup>20a</sup> means a hydrogen atom, a halogen atom or a pseudohalogen.

*Sub A*  
8. Pharmaceutical compositions that contain at least one 17-methylene steroid according to claim 1, 2, 3, 4 or 5, optionally together with pharmaceutically compatible adjuvants and vehicles.

9. 17-Methylene steroids according to one of claims 1 to 5 for use as therapeutic active ingredients.

10. Use of the compounds according to one of claims 1 to 5 for treatment of prostate diseases, alopecia of the male type, acne and hirsutism, for contraception in men and women and/or for inhibition of 5 $\alpha$ -reductase.

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